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(54) Title: EDIBLE FILMS AND COATINGS

(57) Abstract

Edible films and coatings suitable for use as moisture barriers in food (such as multi component foods), emulsions and dry mixes for preparing such films, foods incorporating them and processes for producing them.

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EDIBLE FILMS AND COATINGS

Field of the invention

The present invention relates to edible films and coatings which are suitable for use as moisture barriers in foods (such as multicomponent foods), to emulsions and dry mixes for preparing such films, to foods incorporating them and to processes for producing the films, emulsions, mixes and foods. In particular, the invention relates to films comprising lipid and hydrocolloid conglomerates in which the lipid component is derived from an dried fat composition and/or the hydrocolloid component comprises a starchy leguminous seed protein (such as pea protein).

Composite foods

Many foods are heterogeneous, in that they consist of different components having different textural and organoleptic qualities. In most cases, the various components have different moisture levels. Examples of such food products include pizzas (in which a moist topping is associated with a crisp base), pies (in which a moist filling is held within a relatively dry crust), quiches and crumbles.

An important determinant of the quality and mouthfeel of such foods is the contrast between the textural qualities of the

different components. Particularly important in this respect are the relative moisture contents of the different components.

However, it has long been known that after preparation and on storage of multicomponent foods, the moisture levels of the various different components tend to equilibrate. Moreover, the relatively dry food components may also take up water from the environment.

These changes in water content lead to significant and deleterious changes in the textural and organoleptic properties of the foodstuff. In particular, the changes in water distribution within the food leads to sogginess, spoiling, reduced shelf-life, impaired mouthfeel and discolouration.

These problems are often exacerbated during cooking, since moisture then migrates at an even faster rate from the wetter domains of the food to the drier. This problem is particularly acute with microwaveable products where the relatively short cooking times are insufficient to drive off gained water in the drier food components.

Edible moisture barriers

There is therefore a need to stabilize the moisture gradients and preserve moisture content discontinuities within multi-component foods so that the different textural and organoleptic qualities of the various different food components can be maintained.

To this end, various different types of edible films and coatings suitable for use as moisture barriers in multicomponent foods have been developed.

In general, edible films and coatings can be divided into three classes: hydrocolloids, lipids and composites. Typical hydrocolloids include proteins, cellulose derivatives, plant gums (such as alginates and pectins), starches and other polysaccharides. Typical lipids include waxes, acylglycerols and fatty acids. Composite films contain both lipid and hydrocolloid components.

A composite film can be formulated as a bilayer in which one layer is a hydrocolloid and the other a lipid, or as a conglomerate in which the lipid and hydrocolloid components are interspersed throughout the film.

Conglomerate films can be particularly effective as moisture barriers, since the lipid component acts as a hydrophobic barrier while the hydrocolloid component(s) act as a supporting matrix which imparts structural stability to the film and prevents breakdown of the lipid barrier. In the absence of a supporting matrix, lipid layers alone cannot form robust, continuous films or coatings. Thus, the hydrocolloid component(s) help maintain the physical integrity of the barriers during subsequent food processing, storage and/or cooking.

Hydrocolloid components known to be suitable for use in conglomerate films include carbohydrates and proteins. Suitable film-forming proteins include gelatin, casein, soy protein, whey protein, wheat gluten and zein. Suitable film-forming carbohydrates include starches, plant gums and chemically modifies starches.

Charged hydrocolloids can be very useful for film formation: alginates and pectins gel on the addition of polyvalent ions (usually calcium).

WO 87/03453 describes an edible laminated (layered) film for retarding water transfer among components of a multicomponent food product. The film includes a base film having a hydrophilic polymer layer and a base film lipid layer. The base film lipid layer has a hydrophobic surface presented away from the hydrophilic polymer layer and an additional lipid layer laminated to the hydrophobic surface of the base film lipid layer.

GB 2 262 245 describes an edible moisture barrier laminated film suitable for use in various food products. The film comprises an edible insoluble fibrous protein and an edible polysaccharide having a coating of an edible hydrophobic material on at least a portion of a surface thereof.

US 4 293 572 discloses a water in oil emulsion or colloidal dispersion prepared from an emulsified triglyceride or an emulsifier only in combination with an aqueous solution of

dextrin or other soluble saccharide or polysaccharide. The emulsion, prepared by the addition of heat and agitation, is thereafter applied to the surface of a food product and allowed to set, after which further processing of the food may be effected.

GB 2 242 815 describes a conglomerate barrier coating comprising a mixture of an edible fat and a milk protein in the form of a membrane. The coating preferably comprises a melted dispersion of full cream milk powder and sugar in cocoa butter. The barrier may be used, like those of the present invention, in the preparation of a heterogeneous food product containing components of different water activities comprising applying a dispersion of the moisture barrier coating onto one of the food components and then forming the two food components into the heterogeneous food product. The amount of coating used is selected to be effective to retard moisture migration from the food component with the higher water activity into the coated food component.

EP 0 638 488 describes an edible moisture barrier suitable for use with microwaved food products. The barrier comprises a carbohydrate sheet support carrying a water-repellent lipid layer. The barrier dissolves and/or melts on heating.

WO 86/00501 discloses an edible pre-formed film for retarding moisture transfer among components of food having different vapor pressures, comprising a hydrophilic polymer layer and a

lipid layer adhered to the hydrophilic polymer layer such that the film has a thickness in the range 0.035 to 0.150 mm. The exposed surface of the lipid layer is oriented toward the higher vapour pressure component of the food such that when the film is placed between components of a food having different vapour pressures, the film can retard moisture transfer between the food components.

However, despite the extensive literature describing moisture barriers and the considerable commercial importance attached to them, there is still a need for a moisture barrier film suitable for use in multicomponent foodstuffs which is easy to apply, does not require heating prior to application and which is robust enough to withstand cooking or heating (e.g. microwave cooking or heating).

Description of the invention

According to a first aspect of the present invention there is provided an edible composite film or coating for use as a moisture barrier in a foodstuff, the film comprising a conglomerate of lipid and hydrocolloid components wherein the lipid component is derived from an dried fat composition.

The term "dried fat composition" is used herein to define fat preparations (often in powder form) which have been produced by solidifying a fat emulsion or suspension, usually in the

presence of a carrier. Most dried fat compositions are spray dried emulsions of fat in association with protein and/or carbohydrate carriers. A wide variety of different dried fat compositions are commercially available.

The dried fat compositions of the invention are used as a lipid source in the edible films. In this capacity, they have been found to exhibit surprising advantages. As used herein, the term fat is intended to encompass oils and processed fats.

Without wishing to be bound by any theory, it is thought that the finely dispersed fat particles present in dried fat compositions very efficiently form emulsions or suspensions when mixed at room temperatures as part of an aqueous system. This permits the production of films in which the lipid component is evenly distributed throughout the film matrix, which leads to improved moisture barrier properties.

The fat in the dried fat composition may be in association with a carrier. Preferably, the carrier is a gum and/or a protein (e.g. milk protein) and/or carbohydrate (e.g. lactose or maltodextrin or starch) carrier.

In preferred embodiments, the dried fat composition comprises 50-80% fat (e.g. about 75%); 10-30% carbohydrate (e.g. about 15%); and 2-25% protein (e.g. about 10%). They may also include emulsifiers, stabilizers, free-flowing agents and preservatives.

Preferably, the fat in the dried fat composition is capable of forming a uniform micro-emulsion or micro-suspension when mixed with high shear at 20-30° C.

The kinetic energy imparted to the fat by the use of high shear mixing conditions effectively promotes dispersion of the fat. Thus, the dried fat compositions of the invention can be used as the basis of effective emulsions or dispersions without the need for heating a mixture of fat and hydrocolloid in the preparation of an initial emulsion.

The hydrocolloid component preferably comprises (or consists of) a starchy leguminous seed protein. The term "starchy leguminous seed protein" is a term of art which is used in contradistinction to the non-starch leguminous seeds typical of the *Lupinae* and *Glycinae* subfamilies (to which the lupin and soybean species belong). The starchy leguminous seed proteins include those derived from representatives of the *Viciae* and *Phaseolae* subfamilies (for example, the pea and fababean species).

The starchy leguminous seed proteins (particularly pea proteins) have been found to be particularly useful as hydrocolloid components in the film of the invention, because they exhibit good gel forming properties without imparting excessive viscosity to the emulsion used as an intermediate in the production of the films of the invention (see *infra*). This

significantly improves the handling characteristics of the emulsion, facilitating its application to various foods. They are particularly advantageous when the emulsion is to be applied to a food product by spraying.

A particularly preferred starchy leguminous seed protein for use according to the invention is pea protein.

The proteins for use in the present invention need not be pure preparations, but can be provided as crude isolates or concentrates. In general, the proteins used in the invention are more or less complex heterogeneous mixtures of different protein species. Thus, the pea protein for use in the invention may comprise any of a number of different pea protein fractions.

The edible film preferably comprises (or consists of) a conglomerate of a lipid component (e.g. derived from an dried fat composition), a protein component, a gelled plant gum, an emulsifier, and optionally a buffering agent and/or plasticiser.

In a second aspect, the invention provides an edible composite film for use as a moisture barrier in a foodstuff, the film comprising a conglomerate of lipid and hydrocolloid components wherein the hydrocolloid component comprises (or consists of) a starchy leguminous seed protein, or lupin protein.

Preferably, the starchy leguminous seed protein is a pea protein and the lipid component is derived from an dried fat composition.

The film may comprises (or consists of) a conglomerate of a lipid component (e.g. derived from an dried fat composition), a protein component, a gelled plant gum, an emulsifier and optionally a buffering agent and/or a plasticiser.

In a third aspect, the invention relates to an edible composite film for use as a moisture barrier in a foodstuff, the film comprising (or consisting of) a conglomerate of: a lipid component; a protein component; a gelled plant gum; an emulsifier; water; and optionally a buffering agent and/or a plasticiser.

The term lipid is intended to encompass neutral lipids of glycerides (esters of glycerol and fatty acids) and waxes (esters of long chain monohydric alcohols and fatty acids). Particularly preferred lipids for use in the invention include hydrophobic compounds such as fats, oils, acetylated monoglycerides, polyglycerides, acylglycerols, fatty acids and waxes.

In preferred embodiments, the lipid component for use in the present invention may comprise soya, palm or coconut (e.g. hydrogenated soya, palm or coconut) fats, butter fat, milk fat, palm kernel oil, sunflower seed oil, rapeseed oil, cocoa butter, lard, fish oil, cottonseed oil, olive oil, groundnut oil and their processed counterparts or derivatives.

The lipid component is preferably derived from an dried fat composition, while the protein component may comprise a starchy leguminous seed protein (for example, a pea protein).

The films or coatings of the invention may contain a lipid or lipid source (e.g. an dried fat composition) at: 20-40%; 21-39%; 22-38%; 23-37%; 24-36%; 25-35%; 26-34%; 27-33%; 28-32%; 29-31%; or about 30%. They may contain protein at: 1-35%; 1-25%; 1-20%; 1-18%; 1-14%; 1-13%; 1-12%; 1-11%; 2-16%; 3-15%; 4-14%; 5-13%; 6-12%; 5-11%; 6-10%; 7-9% or about 8%. They may contain gelled plant gum at: 0.1-5.%; 0.1-3.2%; 0.1-3.0%; 0.1-2.8%; 0.1-2.6%; 0.1-2.4%; 0.1-2.2%; 0.1-2.0%; 0.1-1.9%; 0.1-1.8%; 0.1-1.7%; 0.1-1.6%; 0.1-1.5%; 0.2-1.4%; 0.3-1.3%; 0.4-1.2%; 0.5-1.1%; 0.5-1.0%; 0.5-0.9%; 0.5-0.8%; 0.6-0.7%; or about 0.65%. They may contain plasticiser at: 0-14%; 1-13%; 2-12%; 3-11%; 4-10%; 5-9%; 6-8%; or about 7%. They may contain emulsifier at: 0.1-2.0%; 0.1-1.9%; 0.1-1.8%; 0.1-1.7%; 0.1-1.6%; 0.1-1.5%; 0.1-1.4%; 0.1-1.2%; 0.1-1.1%; 0.1-1.0%; 0.2-0.9%; 0.3-0.8%; 0.4-0.7%; 0.5-0.6%; or about 0.55%. They may contain buffering agent at: 0.1-2.0%; 0.1-1.9%; 0.1-1.8%; 0.1-1.7%; 0.1-1.6%; 0.1-1.5%; 0.1-1.4%; 0.1-1.2%; 0.1-1.1%; 0.1-1.0%; 0.2-0.9%; 0.3-0.8%; 0.4-0.7%; 0.5-0.6%; or about 0.55%. All percentages are expressed as w/w with respect to the total weight of the ungelled film emulsion or the wet film immediately after gelling or setting.

The dried fat composition for use in the invention is preferably spray dried.

The film of the invention preferably comprises a hydrocolloid component which acts as a supporting matrix for the lipid component.

The hydrocolloid component preferably comprises a protein, such as a film-forming and/or emulsifying protein. It may also comprise a charged hydrocolloid component and/or a gelled plant gum. In preferred embodiments, the hydrocolloid component comprises a mixture of film-forming protein and a gelled plant gum (such as alginate or pectin).

In preferred embodiments, the protein is selected from any one of: gelatin; casein; soy protein; whey protein; wheat gluten; zein; albumen; starchy leguminous seed protein; mixtures of any of the foregoing proteins.

Particularly preferred is pea protein, for example a pea protein isolate or concentrate.

The hydrocolloid component preferably comprises: alginate; pectin; carrageenan; cellulose; agar; seaweed extract; mixtures of any of the foregoing.

In preferred embodiments, the gelled plant gum is a low viscosity alginate (e.g. sodium alginate). Such alginates are easily selected

from a wide range of commercially available alginates having different properties. Low viscosity alginates are particularly useful as hydrocolloid components in the film of the invention because they may retain good elastic properties without imparting excessive viscosity to the emulsion used as an intermediate in the production of the films of the invention (see *infra*). This significantly improves the handling characteristics of the emulsion, facilitating its application to various foods. They are particularly advantageous when the emulsion is to be applied to a food product by spraying.

The alginate may advantageously be a highly elastic, medium gel strength alginate. Such alginates are particularly advantageous in conjunction with foods which are subject to physical stress during cooking or preparation, such as microwaveable pies.

The gum may be gelled with a mono-, di- or polyvalent cation, preferably with a calcium ion. The gelling cations for use in the invention may be encapsulated to achieve delayed release of the gelling agents and so prevent premature setting of the emulsion during processing.

In preferred embodiments, the calcium ion is derived from calcium lactate, calcium chloride, calcium carbonate, calcium hydroxide, calcium citrate, calcium ascorbate and hydrated salts thereof.

The film of the invention may further comprise a plasticiser, such as a polyol (e.g. glycerol); and/or sorbitol; and/or ethanolamine; and/or tocopherol; and/or an acetylated monoglyceride; and/or polyethylene glycol; and/or sucrose; and/or phospholipid (eg lecithin).

Preferred plasticisers (such as lecithin) also act as emulsifiers.

The film may also comprise an emulsifier, for example lecithin (e.g. soya lecithin); and/or beeswax; and/or glycerol monostearate; and/or isopropyl palmitate; and/or lauric acid; and/or lauryl alcohol; and/or sodium oleate; and/or potassium oleate; and/or sorbitan monostearate; and/or stearyl alcohol; and/or triethanolamine oleate soap; and/or acetylated monoglycerides; and/or oleic acid; and/or palm oil; and/or fatty acids; and/or glycol monostearates; and/or polyol monostearates.

The film may also comprise a buffering agent (e.g. an acidity regulator). Any of a wide variety of food acceptable buffering agents may be used, and in preferred embodiments the buffering agent is sodium polyphosphate.

The film of the invention may further comprise various minor ingredients which provide incidental functions. For example, the films may include an antimicrobial agent, one or more vitamins, an antioxidant, a flavour, a pigment or mixtures thereof.

The invention also contemplates a dry mix (e.g. in the form of a powder) for use as a hydratable base in the preparation of the film of any one of the preceding claims, the mix comprising lipid and hydrocolloid sources, wherein: the lipid source comprises (or consists of) an dried fat composition; and/or the hydrocolloid source comprises (or consists of) a starchy leguminous seed protein; and/or the mix comprises (or consists of): (i) a lipid source (e.g. an dried fat composition); and (ii) a protein component (e.g. a starchy leguminous seed protein); and (iii) a gellable plant gum; and (iv) an emulsifier.

Preferably, the dry mix of the invention further comprises a buffering agent; and/or a plasticiser; and/or a gelling salt.

The gelling salt is preferably a source of mono-, di- or polyvalent ions. In preferred embodiments, the gelling salt is a calcium salt, for example a sparingly soluble calcium salt (e.g. calcium lactate, calcium carbonate or calcium hydroxide, calcium chloride and/or an encapsulated gelling agent) which gels the plant gum after a time delay (e.g. of 30 to 1200 seconds) following hydration of the mix.

The use of such sparingly soluble calcium salts effectively permits "timed release" of the gelling ions into the emulsion, so obviating the need for a separate setting stage (involving for example spraying a solution of the gelling salt onto the emulsion-coated foodstuff) whilst allowing time for the emulsion to be easily applied to the food (e.g. by spraying).

In preferred embodiments, the dry mix comprises a lipid source present at: 40-80%; 42-78%; 44-76%; (iv) 46-74%; 48-72%; 50-70%; 52-68%; 54-66%; 56-64%; 58-62%; or about 60%. All percentages are expressed as w/w with respect to the total weight of the dry mix.

The mix may comprises a protein component (e.g. a starchy leguminous seed protein). In such embodiments, the protein may be present at: 2-70%; 2-28%; 2-26%; 2-24%; 2-22%; 4-20%; 6-18%; 8-16%; 10-12%; about 11%. All percentages are expressed as w/w with respect to the total weight of the dry mix.

Preferably, the mix comprises a gellable plant gum, for example at: 0.2-10.0%; 0.2-6.4%; 0.2-6.0%; 0.2-5.6%; 0.2-5.2%; 0.2-4.8%; 0.2-4.4%; 0.2-4.0%; 0.2-3.8%; 0.2-3.6%; 0.2-3.4%; 0.2-3.2%; 0.2-3.0%; 0.4-2.8%; 0.6-2.6%; 0.8-2.4%; 1.0-2.2%; 1.0-2.0%; 1.0-1.8%; 1.0-1.6%; 1.2-1.4%; about 1.3%. All percentages are expressed as w/w with respect to the total weight of the dry mix.

The mix may also comprise an emulsifier, for example present at: 0.2-4.0%; 0.2-3.8%; 0.2-3.6%; 0.2-3.4%; 0.2-3.2%; 0.2-3.0%; 0.2-2.8%; 0.2-2.4%; 0.2-2.2%; 0.2-2.0%; 0.4-1.8%; 0.6-1.6%; 0.8-1.4%; 1.0-1.2%; about 1%. All percentages are expressed as w/w with respect to the total weight of the dry mix.

Preferably, the dry mix also comprises a buffering agent, e.g. present at: 0.2-4.0%; 0.2-3.8%; 0.2-3.6%; 0.2-3.4%; 0.2-3.2%; 0.2-3.0%; 0.2-2.8%; 0.2-2.4%; 0.2-2.2%; 0.2-2.0%; 0.4-1.8%; 0.6-1.6%; 0.8-1.4%; 1.0-1.2%; about 1%. All percentages are expressed as w/w with respect to the total weight of the dry mix.

The hydrocolloid source for use in the dry mix of the invention may be a gellable plant gum or charged hydrocolloid source, for example a hydrocolloid source which gels to form a hydrocolloid component as hereinbefore defined.

Where present, the emulsifier may be as hereinbefore defined. The mix may further comprise a buffering agent, for example as hereinbefore defined. Advantageously, the mix further comprises an antimicrobial agent, one or more vitamins, an antioxidant, a flavour, a pigment or mixtures thereof.

The invention also contemplates a moisture barrier system (e.g. a kit for preparing a moisture barrier for use in a foodstuff) comprising, as separate components: the dry mix of the invention as hereinbefore defined and a gelling salt solution.

The moisture barrier system may optionally further comprise a liquid plasticiser (e.g. a polyol, such as glycerol, or any of the other plasticisers as hereinbefore defined. In such embodiments, the film may is produced by first preparing a dry mix of lipid and

hydrocolloid components and then adding water and glycerol to produce an emulsion. The emulsion may then be set or gelled by the addition of gelling salt (or by the slow release of sparingly soluble gelling salt-derived ions solubilized from the dry mix after the addition of water).

The gelling salt solution is preferably a calcium salt solution, for example a gelling salt solution at 1-10% w/v. The gelling salt solution preferably contains mono-, di- or polyvalent cations (for example a calcium salt). Particularly preferred is a solution of calcium chloride (e.g. at about 5% w/v).

In another aspect, the invention provides an emulsion or suspension (e.g. a microemulsion or microsuspension) comprising the dry mix of the invention in admixture with water (for example at about 50-60% w/w). In such emulsions/suspensions, the gellable plant gum is preferably in an ungelled state.

The emulsion of the invention may be formulated such that no gelling salt is present. Such emulsions may have a low viscosity, making them convenient to handle and easy to apply to a foodstuff. They can be set or gelled into stable films or coatings by contacting them with a gelling salt, conveniently in a separate processing step. The gellable plant gum present in the emulsion/suspension will then set or gel to provide a robust matrix which supports the lipid component, so forming a stable moisture barrier *in situ*.

The invention also contemplates a foodstuff comprising the film or emulsion of the invention. Preferred foodstuffs include baked foodstuffs, cold eating pies (for example apple pie), hot eating pie (for example meat pie, e.g. pork pie), savoury pie, pizza, turnover, cake, quiche, topped doughnut, filled pastries and ice creams in cones.

The invention also embraces a process for producing the edible composite film of the invention comprising the steps of preparing a dry mix as hereinbefore defined and then hydrating the dry mix to produce an emulsion (or suspension) as hereinbefore defined. The process may be a two stage process, further comprising the step of gelling the emulsion to produce the film.

The dry mix is preferably hydrated by high shear mixing with water.

The emulsion for use in the process of the invention preferably comprises ungelled plant gum.

The dry mix preferably comprises a gelling salt and the plant gum may then be gelled when the gelling salt is dissolved on hydration of the dry mix. In such embodiments, complete gelling may be achieved between 30 and 1200 seconds after mixing. This facilitates handling of the emulsion prior to (and during) application to the foodstuff, while obviating the need for a separate gelling step (e.g. involving the addition of gelling salt) *in situ*.

In another embodiment of the process of the invention, the dry mix does not include a gelling salt and the plant gum is gelled by adding a gelling salt solution to the emulsion. In such embodiments, the gelling salt solution is preferably sprayed onto the emulsion.

The emulsion may be cast to yield a shaped self-supporting film. In such embodiments, the emulsion may be cast, cut or formed into various shapes (e.g. a disc shape). Such films find particular application in the production of pie bases, ice cream cones, pastry bases or pizza crusts.

Also contemplated by the invention is a process for preparing a foodstuff comprising the steps of producing an edible composite film by the process as defined above and then applying the film to the foodstuff.

In another aspect, the invention contemplates a process for preparing a foodstuff comprising the steps of producing an emulsion comprising ungelled plant gum as defined above, applying the emulsion to the foodstuff and then gelling the plant gum in the emulsion to produce an edible composite film which acts as a moisture barrier in the foodstuff.

According to this latter aspect of the invention, the plant gum may be gelled by cations present in the emulsion or by contacting the emulsion with a gelling salt *in situ*.

The emulsion/suspension of the invention may be applied to the foodstuff by any convenient method, for example by spraying, brushing, ladling, dipping, casting, pouring, spreading, panning, enrobing or rolling.

The invention also contemplates a method for preventing the transfer of moisture between constituents of a multi-component food product comprising the step of interposing the film of the invention between the food constituents.

The film may be interposed between the food constituents by providing a first food constituent, applying the film to the first constituent and then providing a second food constituent to produce a multi-component food product in which the film is interposed between the first and second constituent.

Alternatively, the film may be wrapped about a foodstuff or applied thereon as a coating to prevent moisture transfer between the foodstuff and the atmosphere.

The film is preferably interposed between the food constituents by the steps of: providing a first food constituent; applying an emulsion or suspension as hereinbefore defined to the first constituent; gelling the emulsion to produce a film as hereinbefore defined; and then providing a second food constituent to produce a multi-component food product in which the film is interposed between the first and second constituents.

Examples

The invention will now be described in more detail with reference to several examples. These examples are for illustrative purposes only and are not intended to limit the scope of the invention in any way.

Determination of water vapour transmission

This was measured a gravimetric technique involving sealing the test film mounted on a sheet of filter paper over the mouth of a test dish containing a dessicant. The assembly is then placed in a chamber at a controlled humidity level of 65% at 5°C. Periodic weighings determine the rate of water transmission through the specimen. The WVT values reported herein are based on film thicknesses of 0.4 mm.

Example 1

An emulsion was made to the following recipe:

soya protein	:	5.25%
Satro™ fat	:	29.75%
lecithin	:	0.51%
tetron	:	0.51%
alginate	:	0.61%
glycerol	:	7.00%

water : 56.37%

Satro™ fat is a spray dried fat composition of hardened vegetable fat containing 72.5% fat, 10.0% protein and 13.7% carbohydrates. Satro FP72™ was used.

The emulsion was prepared by first dry mixing the lecithin, tetron, alginate, fat and soya protein to form a uniform, free flowing dry mix.

This dry mix was then mixed with glycerol and water at ambient temperature (about 22°C) using a Silverson™ mixer to form a stable, homogeneous emulsion. The emulsion was then brushed onto an apple pie base.

The emulsion was set *in situ* by spraying a small quantity of 5% $CaCl_2$ in water onto the emulsion on the pie base. After air drying for five minutes, apple filling was added and the pie baked.

The viscosity of the emulsion was 7800 centipoise. The WVT (g/s.m.m) was 0.0006. The film was robust and effectively prevented migration of moisture in the apple filling into the pie crust.

Example 2

A film was prepared as described in Example 1, except that whey protein was used instead of the soya protein. The viscosity

of the emulsion was 6000 centipoise. The WVT (g/s.m.m) was 0.0010. The film was robust and effectively prevented migration of moisture in the apple filling into the pie crust.

Example 3

A film was prepared as described in Example 1, except that casein was used instead of the soya protein. The viscosity of the emulsion was 12400 centipoise. The WVT (g/s.m.m) was 0.0005. The film was robust and effectively prevented migration of moisture in the apple filling into the pie crust.

Example 4

A film was prepared as described in Example 1, except that albumen was used instead of the soya protein. The viscosity of the emulsion was 6600 centipoise. The WVT (g/s.m.m) was 0.0005. The film was robust and effectively prevented migration of moisture in the apple filling into the pie crust.

Example 5

A film was prepared as described in Example 1, except that pea was used instead of the soya protein. The viscosity of the emulsion was 5000 centipoise, and the emulsion was applied to the pie crust by spraying. The WVT (g/s.m.m) was 0.0003. The film was robust and effectively prevented migration of moisture in the apple filling into the pie crust.

Example 6

A film was prepared as described in Example 1, except that gluten was used instead of the soya protein. The viscosity of the emulsion was 1300 centipoise, and the emulsion was applied to the pie crust by spraying. The WVT (g/s.m.m) was 0.0006. The film was robust and effectively prevented migration of moisture in the apple filling into the pie crust.

Example 7

A film was prepared as described in Example 1, except that pectin was used instead of the alginate. The performance was similar, except that the film was somewhat less robust.

Example 8

A film was prepared as described in Example 1, except that De Kievit Grasa 60A118™ was used instead of the Satro™.

This fat is a spray dried suspension of hydrogenated soya at 60%, carbohydrate at 30% and protein at 5%.

The viscosity of the emulsion was 8800 centipoise, and the emulsion was applied to the pie crust by brushing. The WVT (g/s.m.m) was 0.0013. The film was robust and effectively

prevented migration of moisture in the apple filling into the pie crust.

Example 9

A film was prepared as described in Example 1, except that De Kievit Crema 72D™ was used instead of the Satro™.

This fat is a spray dried suspension of hydrogenated soya at 72%, carbohydrate at 15% and protein at 9%.

The viscosity of the emulsion was 18600 centipoise, and the emulsion was applied to the pie crust by brushing. The WVT (g/s.m.m) was 0.00093. The film was robust and effectively prevented migration of moisture in the apple filling into the pie crust.

Example 10

A film was prepared as described in Example 1, except that De Kievit Lata 50D™ was used instead of the Satro™.

This fat is a spray dried suspension of coconut oil at 50%, carbohydrate at 26% and protein at 18%.

The viscosity of the emulsion was 9200 centipoise, and the emulsion was applied to the pie crust by brushing. The WVT (g/s.m.m) was 0.00029. The film was robust and effectively

prevented migration of moisture in the apple filling into the pie crust.

Example 11

A film was prepared as described in Example 1, except that De Kievit Lata 70H™ was used instead of the Satro™.

This fat is a spray dried suspension of hydrogenated coconut oil at 70%, carbohydrate at 15% and protein at 10%.

The viscosity of the emulsion was 58000 centipoise, and the emulsion was applied to the pie crust by brushing. The WVT (g/s.m.m) was 0.0050. The film was robust and effectively reduced migration of moisture in the apple filling into the pie crust.

Example 12

An emulsion was made to the following recipe:

gluten protein	:	5.00%
Satro™ fat	:	25.00%
lecithin	:	0.50%
tetron	:	0.50%
alginate	:	0.60%
glycerol	:	7.00%
water	:	61.00%

Satro FP72™ was used.

The emulsion was prepared by first dry mixing the lecithin, tetron, alginate, fat and gluten protein to form a uniform, free flowing dry mix.

This dry mix was then mixed with glycerol and water at ambient temperature (about 22°C) using a Silverson™ mixer to form a stable, homogeneous emulsion. The emulsion was then brushed onto an apple pie base.

The emulsion was set *in situ* by spraying a small quantity of 5% $CaCl_2$ in water onto the emulsion on the pie base. After air drying for five minutes, apple filling was added and the pie baked.

The viscosity, WVT (g/s.m.m) and film characteristics were similar to that described for Example 6.

Example 13

A film was prepared as described in Example 12, except that pea was used instead of the gluten protein. The viscosity, WVT (g/s.m.m) and film characteristics were similar to that described for Example 5.

Example 14

An emulsion was made to the following recipe:

pea protein	:	5.00%
Satro ™ fat*	:	30.00%
lecithin	:	1.00%
citric acid	:	0.50%
alginate	:	1.50%
glycerol	:	7.00%
water	:	54.00%

A film was prepared as described in Example 1. The viscosity, WVT (g/s.m.m) and film characteristics were similar to that described for Example 1.

Example 15

A film was prepared as described in Example 14 except that the emulsion was set by mixing with a solution of 50% $CaSO_4$ and 0.25% xanthan gum.

CLAIMS

1. An edible composite film for use as a moisture barrier in a foodstuff, the film comprising a conglomerate of lipid and hydrocolloid components wherein the lipid component is derived from an dried fat composition.

2. The edible film of claim 1 wherein the hydrocolloid component comprises (or consists of) a starchy leguminous seed protein.

3. The edible film of claim 1 or claim 2 which comprises (or consists of) a conglomerate of:
(a) a lipid component (e.g. derived from an dried fat composition);
(b) a protein component;
(c) a gelled plant gum;
(d) an emulsifier; and optionally
(e) a buffering agent and/or a plasticiser.

4. An edible composite film for use as a moisture barrier in a foodstuff, the film comprising a conglomerate of lipid and hydrocolloid components wherein the hydrocolloid component comprises (or consists of) a starchy leguminous seed protein or lupin protein.

5. The edible film of claim 4 wherein the lipid component is derived from an dried fat composition.

6. The edible film of claim 4 or claim 5 which comprises (or consists of) a conglomerate of:

(a) a lipid component (e.g. derived from an dried fat composition);

(b) a protein component;

(c) a gelled plant gum;

(d) an emulsifier; and optionally

(e) a buffering agent and/or plasticiser

7. An edible composite film for use as a moisture barrier in a foodstuff, the film comprising (or consisting of) a conglomerate of:

(a) a lipid component;

(b) a protein component;

(c) a gelled plant gum;

(d) an emulsifier;

(e) water; and optionally

(f) a buffering agent, and/or plasticiser.

8. The edible film of claim 7 wherein the lipid component is derived from an dried fat composition.

9. The edible film of claim 7 or claim 8 wherein the protein component comprises a starchy leguminous seed protein.

10. The film of any one of the preceding claims wherein the lipid or lipid source (e.g. an dried fat composition) is present at:

(a) 20-40%; or

(b) 21-39%; or

(c) 22-38%; or

(d) 23-37%; or

(e) 24-36%; or

(f) 25-35%; or

(g) 26-34%; or

(h) 27-33%; or

(i) 28-32%; or

(j) 29-31%; or

(k) about 30%.

11. The film of any one of the preceding claims wherein protein is present at 1-35%; or 1-25% or 1-20% or 1-18% or 1-14% or 1-13% or 1-12% or 1-11% or 2-16% or 3-15% or 4-14% or 5-13% or 6-12% or 5-11% or 6-10% or 7-9% or about 8%.

12. The film of any one of the preceding claims wherein gelled plant gum is present at:

(a) 0.1-5.0%; or

(b) 0.1-3.2%; or

(c) 0.1-3.0%; or

(d) 0.1-2.8%; or

(e) 0.1-2.6%; or

(f) 0.1-2.4%; or

(g) 0.1-2.2%; or

(h) 0.1-2.0%; or

(i) 0.1-1.9%; Or

(j) 0.1-1.8%; or

(k) 0.1-1.7%; or

(l) 0.1-1.6%; or

(m) 0.1-1.5%; or

(n) 0.2-1.4%; or

(o) 0.3-1.3%; or

(p) 0.4-1.2%; or

(q) 0.5-1.1%; or

(r) 0.5-1.0%; or

(s) 0.5-0.9%; or

(t) 0.5-0.8%; or

(u) 0.6-0.7%; or

(v) about 0.65%.

13. The film of any one of the preceding claims wherein plasticiser is present at:

(a) 0-14%; or

(b) 1-13%; or

(c) 2-12%; or

(d) 3-11%; or

(e) 4-10%; or

(f) 5-9%; or

(g) 6-8%; or

(h) about 7%.

14. The film of any one of the preceding claims wherein emulsifier is present at up to 10%, for example at:

(a) 0.1-2.0%; or

(b) 0.1-1.9%; Or

(c) 0.1-1.8%; or

(d) 0.1-1.7%; or

(e) 0.1-1.6%; or

(f) 0.1-1.5%; or

(g) 0.1-1.4%; or

(c) 0.1-1.2%; or

(d) 0.1-1.1%; or

(e) 0.1-1.0%; or

(f) 0.2-0.9%; or

(g) 0.3-0.8%; or

(h) 0.4-0.7%; or

(i) 0.5-0.6%; or

(j) about 1.5% or

(k) about 0.55%

15. The film of any one of the preceding claims wherein buffering agent is present at:

(a) 0.1-2.0%; or

(b) 0.1-1.9%; Or

(c) 0.1-1.8%; or

(d) 0.1-1.7%; or

(e) 0.1-1.6%; or

(f) 0.1-1.5%; or

(g) 0.1-1.4%; or

(c) 0.1-1.2%; or

(d) 0.1-1.1%; or

(e) 0.1-1.0%; or

(f) 0.2-0.9%; or

(g) 0.3-0.8%; or

(h) 0.4-0.7%; or

(i) 0.5-0.6%; or

(j) about 0.55%.

16. The film of any one of the preceding claims which comprises a lipid component derived from an dried fat composition.

17. The film of claim 16 wherein the dried fat composition comprises a spray dried dried fat composition.

18. The film of claim 16 or 17 wherein the fat in the dried fat composition is in association with a carrier.

19. The film of claim 18 wherein the carrier is a gum and/or a protein (e.g. milk protein) and/or carbohydrate (e.g. lactose or maltadextrin or starch) carrier.

20. The film of claim 19 wherein the dried fat composition comprises:

(a) 50-80% fat (e.g. about 75%);

(b) 10-30% carbohyrate (e.g. about 15%);

(c) 2-25% protein (e.g. about 10%).

21. The film of any one of claims 16-20 wherein the fat in the dried fat composition is capable of forming a uniform micro-

emulsion or micro-suspension when mixed with high shear at 20-30°C.

22. The film of any one of the preceding claims wherein the lipid component comprises soya, palm or coconut (e.g. hydrogenated soya, palm or coconut) fats, butter fat, milk fat, palm kernel oil, sunflower seed oil, rapeseed oil, cocoa butter, lard, fish oil, cottonseed oil, olive oil, groundnut oil, and their processed counterparts or derivatives.

23. The film of any one of the preceding claims which comprises a hydrocolloid component which acts as a supporting matrix for the lipid component.

24. The film of claim 22 or 23 wherein the hydrocolloid component comprises a protein.

25. The film of claim 24 wherein the protein is a film-forming and/or emulsifying protein.

26. The film of claim 25 wherein the protein is selected from any one of:

(a) gelatin;

(b) casein;

(c) soy protein;

(d) whey protein;

(e) wheat gluten;

(f) zein;

(g) albumen;

(h) starchy leguminous seed protein;

(i) lupin protein;

(j) mixtures of any of the foregoing proteins.

27. The film of any one of the preceding claims comprising a starchy leguminous seed protein, wherein the protein is derived from a member of the *Viciae* or *Phaseolae* subfamilies (for example a fababean or pea protein, e.g. a pea protein isolate or concentrate.

28. The film of any one of claims 23-27, wherein the hydrocolloid component comprises a charged hydrocolloid component and/or a gelled plant gum.

29. The film of claim 28 wherein hydrocolloid component comprises:

(a) pectin;

(b) carrageenan;

(c) seaweed extract (eg alginate or agar);

(d) chitosan;

(e) cellulose;

(f) derivatives and/or mixtures of any of the foregoing.

30. The film of claim 29 wherein the gelled plant gum is a low viscosity alginate (e.g. sodium alginate).

31. The film of claim 30 wherein the alginate is a highly elastic, medium gel strength alginate.

32. The film of any one of claims 28-31 wherein the gum is gelled with a mono-, di- or polyvalent cation.

33. The film of claim 32 wherein the gum is gelled with a calcium ion.

34. The film of claim 33 wherein the calcium ion is derived from calcium lactate, calcium chloride, calcium carbonate, calcium acetate, calcium ascorbate, calcium citrate, calcium gluconate, calcium hydrogen orthophosphate, calcium sulphate or calcium hydroxide.

35. The film of any one of the preceding claims which comprises a plasticiser.

36. The film of claim 35 wherein the plasticiser comprises:
(a) a polyol (e.g. glycerol); and/or
(b) an acetylated monoglyceride; and/or
(c) polyethylene glycol; and/or
(d) sucrose; and/or
(e) sorbitol; and/or
(f) ethanolamine; and/or
(g) tocopherol; and/or
(h) an acetylated monoglyceride; and/or
(I) polyethylene glycol; and/or

(j) sucrose; and/or

(k) a phospholipid (eg lecithin).

37. The film of claim 35 or claim 36 wherein the plasticiser also acts as an emulsifier.

38. The film of any one of the preceding claims comprising an emulsifier.

39. The film of claim 38 wherein the emulsifier comprises:

(a) lecithin (e.g. soya lecithin); and/or

(b) beeswax; and/or

(c) glycerol monostearate; and/or

(d) isopropyl palmitate; and/or

(e) lauric acid; and/or

(f) lauryl alcohol; and/or

(g) sodium oleate; and/or

(h) potassium oleate; and/or

(i) sorbitan monostearate; and/or

(j) stearyl alcohol; and/or

(k) triethanolamine oleate soap and/or

(l) acetylated monoglycerides; and/or

(m) oleic acid; and/or

(n) palm oil; and/or

(o) fatty acids; and/or

(p) glycol monostearates; and/or

(q) polyol monostearates.

40. The film of any one of the preceding claims comprising a buffering agent (e.g. an acidity regulator).

41. The film of claim 40 wherein the buffering agent is sodium polyphosphate.

42. The film of any one of the preceding claims comprising an antimicrobial agent, one or more vitamins, an antioxidant, a flavour, a pigment or mixtures thereof.

43. A dry mix (e.g. in the form of a powder) for use as a hydratable base in the preparation of the film of any one of the preceding claims, the mix for example comprising lipid and hydrocolloid sources, wherein:

(a) the lipid source comprises (or consists of) an dried fat composition; and/or

(b) the hydrocolloid source comprises (or consists of) a starchy leguminous seed protein; and/or

(c) the mix comprises (or consists of):

(i) a lipid source (e.g. an dried fat composition); and

(ii) a protein component (e.g. a starchy leguminous seed protein); and

(iii) a gellable plant gum; and

(iv) an emulsifier.

44. The dry mix of claim 43(c) further comprising:

(v) a buffering agent; and/or

(vi) a plasticiser; and/or

(vii) a gelling salt.

45. The dry mix of claim 44 wherein the gelling salt is:

(a) a source of mono-, di- or polyvalent ions; and/or

(b) a calcium salt, for example a sparingly soluble calcium salt (e.g. calcium lactate, calcium carbonate or calcium hydroxide) which gels the plant gum after a time delay (e.g. of 30 to 1200 seconds) following hydration of the mix; and/or

c) an acidulant (eg citric acid, d-glucono-lactone) which gels the plant gum after a time delay (eg 2 seconds to 10 minutes) following mixing with a solution of a calcium salt 5-70% (eg calcium sulphate, calcium lactate) and xanthan gum 0.25%.

46. The dry mix of any one of claims 43-45 wherein:

(a) the lipid source comprises a lipid component as defined in any one of claims 16-22; and/or

(b) the lipid source is present at:

(i) 40-80%; or

(ii) 42-78%; or

(iii) 44-76%; or

(iv) 46-74%; or

(v) 48-72%; or

(vi) 50-70%; or

(vii) 52-68%; or

(viii) 54-66%; or

(ix) 56-64%; or

(x) 58-62%; or

(xi) about 60%; and/or

(c) the mix comprises a protein component (e.g. a starchy leguminous seed protein), for example present at 2-70% or 2-50% or 2-40% or 2-36% or 2-28% or 2-26% or 2-24% or 2-22% or 4-32% or 6-30% or 8-28% or 10-26% or 12-24% or 10-22% or 12-20% or 14-18% or about 16%

(d) the mix comprises a gellable plant gum, for example being present at:

(i) 0.2-10.0%; or

(ii) 0.2-8.4%; or

(iii) 0.2-7.0%;or

(iv) 0.2-5.6%; or

(v) 0.2-5.2%; or

(vi) 0.2-4.8%; or

(vii) 0.2-4.4%; or

(viii) 0.2-4.0%; or

(ix) 0.2-3.8%; or

(x) 0.2-3.6%; or

(xi) 0.2-3.4%; or

(xii) 0.2-3.2%; or

(xiii) 0.2-3.0%; or

(xiv) 0.4-2.8%; or

(xv) 0.6-2.6%; or

(xvi) 0.8-2.4%; or

(xvii) 1.0-2.2%; or

(xviii) 1.0-2.0%; or

(xix) 1.0-1.8%; or

(xx) 1.0-1.6%; or

(xxi) 1.2-1.4%; or

(xxii) about 1.3%; and/or

(e) the mix comprises an emulsifier, for example present at up to 20%, for example at:

(i) 0.2-4.0%; or

(ii) 0.2-3.8%; or

(iii) 0.2-3.6%; or

(iv) 0.2-3.4%; or

(v) 0.2-3.2%; or

(vi) 0.2-3.0%; or

(vii) 0.2-2.8%; or

(viii) 0.2-2.4%; or

(ix) 0.2-2.2%; or

(x) 0.2-2.0%; or

(xi) 0.4-1.8%; or

(xii) 0.6-1.6%; or

(xiii) 0.8-1.4%; or

(xiv) 1.0-1.2%; or

(xv) about 3.0%; or

(xvi) about 1%; and/or

(f) the mix comprises a buffering agent, e.g. present at:

(i) 0.2-4.0%; or

(ii) 0.2-3.8%; or

(iii) 0.2-3.6%; or

(iv) 0.2-3.4%; or

(v) 0.2-3.2%; or

(vi) 0.2-3.0%; or

(vii) 0.2-2.8%; or

(viii) 0.2-2.4%; or

(ix) 0.2-2.2%; or

(x) 0.2-2.0%; or

(xi) 0.4-1.8%; or

(xii) 0.6-1.6%; or

(xiii) 0.8-1.4%; or

(xiv) 1.0-1.2%; or

(xv) about 1%; and/or

(g) the mix comprises a hydrocolloid source comprising a protein, for example a protein as defined in any one of claims 25-27; and/or

(h) the hydrocolloid source is a gellable plant gum or charged hydrocolloid source, for example a hydrocolloid source which gels to form a hydrocolloid component as defined in any one of claims 29-34; and/or

(i) the mix comprises an emulsifier, for example as defined in claim 39; and/or

(j) the mix comprises a buffering agent, for example as defined in claim 40 or claim 41; and/or

(k) the mix further comprises an antimicrobial agent, one or more vitamins, an antioxidant, a flavour, a pigment or mixtures thereof; and/or

(l) the mix further comprises a plasticiser.

47. A moisture barrier system (e.g. a kit for preparing a moisture barrier for use in a foodstuff) comprising, as separate components:

(a) a dry mix as defined in any one of claims 43-46; and

(b) a gelling salt solution, and optionally

(c) a liquid plasticiser (e.g. as defined in claim 36 or claim 37).

48. The system of claim 47 wherein the gelling salt solution is a calcium salt solution.

49. The system of claim 47 or claim 48 wherein the gelling salt solution is a 1-10% w/v solution.

50. The system of any one of claims 47-49 wherein the gelling salt solution contains mono-, di- or polyvalent cations (for example a calcium salt).

51. The system of claim 48 wherein the gelling salt solution is a solution of calcium chloride (e.g. at about 5% w/v).

52. An emulsion comprising the dry mix as defined in any one of claims 43-46 in admixture with water (for example at about 50-60% w/w).

53. The emulsion of claim 52 wherein the gellable plant gum is in an ungelled state.

54. The emulsion of claim 53 in which no gelling salt is present.

55. A foodstuff comprising the film as defined in any one of claims 1-42 or emulsion of any one of claims 52-54, or a non-

foodstuff comprising the film as defined in any one of claims 1-42 or emulsion of any one of claims 52-54, for example a pharmaceutical, nutraceutical, wound dressing, incontinence pad, diaper, sanitary towel,tampon or panty liner.

56. The foodstuff of claim 55 which is selected from pasta, confectionery, bakery, snacks, dairy desserts, breakfast cereals, ready meals, biscuits, fruit and vegetables and petfoods, for example a baked foodstuff; a cold eating pie (for example apple pie); a hot eating pie (for example a meat (eg pork) pie); a savoury pie; a pizza; a turnover; a cake (eg a cream cake); a quiche; a topped doughnut; a filled pastry; ice cream (eg in a cone); a nut meat; a pancake; a cream cracker; a crouton; a cheesecake; a crumble; a burger bun; a sausage roll; a sandwich; a wafer; filled pasta; a kiev; fruit pieces in yoghurt or sauces; biscuits; scotch eggs; sausage casings; vegetables in sauces; cottage pies; meringues; crumbs.

57. A process for producing an edible composite film as defined in any one of claims 1-42, comprising the steps of:
(a) preparing a dry mix as defined in any one of claims 43-46;
(b) hydrating the dry mix to produce an emulsion as defined in any one of claims 52-54.

58. The process of claim 57 further comprising the step of:
(c) gelling the emulsion to produce the film.

59. The process of claim 57 or claim 58 wherein the dry mix is hydrated by high shear mixing with water.

60. The process of any one of claims 57-59 wherein the emulsion comprises ungelled plant gum.

61. The process of claim 60 wherein the dry mix comprises a gelling salt and the plant gum is gelled in step (b) when the gelling salt is dissolved on hydration of the dry mix, wherein complete gelling is achieved for example between 30 and 1200 seconds after mixing.

62. The process of claim 60 wherein the dry mix does not include a gelling salt and the plant gum is gelled by adding a gelling salt solution to the emulsion in step (c).

63. The process of claim 62 wherein the gelling salt solution is as defined in any one of claims 48-51.

64. The process of claim 63 wherein the gelling salt solution is sprayed onto the emulsion.

65. The process of any one of claims 57-64 wherein the emulsion is cast to yield a shaped self-supporting film.

66. The process of claim 65 wherein the emulsion is cast into a disc shape, for example for application to pie bases, pastry bases or pizza crusts.

67. A process for preparing a foodstuff comprising the steps of:

(a) producing an edible composite film by a process as defined in any one of claims 57-66;

(b) applying the film to the foodstuff.

68. A process for preparing a foodstuff comprising the steps of:

(a) producing an emulsion comprising ungelled plant gum as defined in any one of claims 52-54 (e.g. by a process as defined in any one of claims 57-66);

(b) applying the emulsion to the foodstuff; and

(c) gelling the plant gum in the emulsion to produce an edible composite film which acts as a moisture barrier in the foodstuff.

69. The process of claim 68 wherein the plant gum is gelled by:

(a) cations present in the emulsion, or

(b) a process as defined in any one of claims 62-64.

70. The process of claim 68 wherein the emulsion is applied to the foodstuff by spraying, brushing, ladling, dipping, casting, pouring, spreading, panning, enrobing or rolling.

71. A method for preventing the transfer of moisture between constituents of a multi-component food product comprising the step of interposing a film as defined in any one of claims 1-42 between the food constituents.

72. The method of claim 71 wherein the film is interposed between the food constituents by:

(a) providing a first food constituent;

(b) applying a film as defined in any one of claims 1-42 to the first constituent;

(c) providing a second food constituent to produce a multi-component food product in which the film is interposed between the first and second constituent.

73. The method of claim 71 wherein the film is interposed between the food constituents by:

(a) providing a first food constituent;

(b) applying an emulsion as defined in any one of claims 52-54 to the first constituent;

(c) gelling the emulsion to produce a film as defined in any one of claims 1-42; and

(d) providing a second food constituent to produce a multi-component food product in which the film produced in step (c) is interposed between the first and second constituent.

74. A method for preventing the transfer of moisture between the atmosphere and a food product comprising the step of interposing a film as defined in any one of claims 1-42 between the food and the atmosphere, eg by coating the food with the film.

75. The process of any one of claims 67-70 or method of any one of claims 71-74 wherein the foodstuff is as defined in claim 56.

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14 January 1999 (14.01.99)

(54) Title: EDIBLE LIPID-PROTEINS FILMS AND COATINGS

(57) Abstract

Edible films and coatings suitable for use as moisture barriers in food (such as multi component foods), emulsions and dry mixes for preparing such films, foods incorporating them and processes for producing them.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/00846

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A23P1/08 A21D13/00 A21D13/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A23P A21D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 547 551 A (NAT STARCH CHEM INVEST) 23 June 1993 see page 2, line 56 - page 5, line 36 see page 8, line 55 - page 10, line 24 see examples see claims --- -/--	1,10,11, 13-15, 22-26, 28,29, 35-44, 46,52, 55,56, 71,72, 74,75

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
10 July 1998	02 11 98

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Vuillamy, V

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/00846

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 465 801 A (NESTLE SA) 15 January 1992 see the whole document	1,8,10, 11,13, 14, 22-26, 35-39, 52,55, 56,71, 72,74,75
X	US 5 019 403 A (KROCHTA JOHN M) 28 May 1991 see column 4, line 21 - column 5, line 12	1,2,4,5, 8-11, 21-26, 52,55, 56,67, 74,75
X	US 5 543 164 A (KROCHTA JOHN M ET AL) 6 August 1996 see column 1, line 1 - column 2, line 26 see column 6, line 7 - line 50 see column 7, line 1 - column 8, line 21 see examples	1,2,4,5, 9-11,13, 22-26, 35-37, 52,55, 56,67, 71,72, 74,75
X	EP 0 594 258 A (FRIESLAND FRICO DOMO COOP) 27 April 1994 see the whole document	1,2,4, 9-11, 22-26, 40-42, 52,55, 56,67, 74,75
X	EP 0 471 558 A (UNILEVER PLC ;UNILEVER NV (NL)) 19 February 1992 see the whole document	1,10,11, 14, 22-26, 28,29, 38,39, 52-56, 67,71, 72,74,75

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/[illegible] 98/00846

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 323 922 A (J.R. DURST) 6 June 1967 see column 1, line 29 - column 3, line 61 see examples ---	1,2,4,5, 8-11,13, 15-29, 35-37, 40, 42-44, 46,52, 55-59, 67,71, 72,74,75
X	FR 2 590 122 A (GEL DOR) 22 May 1987 see page 3, line 1 - page 6, line 18 see examples 1,2 ---	1,7,8, 11,12, 16-26, 28,29, 32, 42-46, 52-61, 65-67, 74,75
X	WO 86 05363 A (BEST CHRISTIAN) 25 September 1986 see page 1, line 1 - line 15 see page 3, line 3 - page 5, line 15 ---	1,3,7,8, 11-15, 22-26, 28,29, 32, 35-40, 42, 52-56, 68,70, 74,75
X	EP 0 643 916 A (UNILEVER NV ;UNILEVER PLC (GB)) 22 March 1995 see claims ---	43,45,46
X	US 4 762 721 A (HOLSCHER EBO J ET AL) 9 August 1988 see column 4, paragraph 2; examples see column 3, paragraph 2 see column 2, line 18 - line 37 --- -/--	1,2,4,5, 9-11,13, 14, 22-26, 38,39, 43,46, 52-57, 67,74,75

INTERNATIONAL SEARCH REPORT

International Application No
PCT/G 98/00846

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 486 076 A (VINK NEE PINCKAERS MARIA AGNES) 20 May 1992 see the whole document ---	1,7, 10-12, 14, 22-25, 28,29, 38,39, 52-56, 67,68, 70,74,75
A	EP 0 048 123 A (MERCK & CO INC) 24 March 1982 see page 2 - page 6 see page 8 see page 10 -----	58-64, 68-70

INTERNATIONAL SEARCH REPORT

Intern nal application No.
PCT/GB 98/ 00846

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see FURTHER INFORMATION SHEET PCT/ISA/210

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-3, 4, 5, 6, 7, 8, 9-15, 16-21, 22-75

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-3, 4 partly, 5, 6 partly, 7 partly, 8, 9-15 all partly, 16-21, 22-75 all partly

In the field of FOODSTUFFS:

- Edible composite film for use as moisture barrier in a FOODSTUFF, the film comprising a conglomerate of lipid and hydrocolloid components, wherein the LIPID COMPONENT is derived from a DRIED FAT COMPOSITION.
- Dry mix for use as a hydratable base in the preparation of the above film.
- Moisture barrier system comprising as separate components, the above dry-mix and a gelling salt solution and opt. a liquid plasticiser.
- Emulsion comprising the above dry-mix in admixture with water.
- FOODSTUFF comprising the above film or emulsion.
- Process for producing an edible composite film as defined above comprising the steps of preparing a dry mix as defined above and hydrating it to produce an emulsion as defined above.
- Process for producing a foodstuff comprising the steps of producing an edible composite film by a process as defined above and applying it to the foodstuff.
- Process for producing a foodstuff comprising the steps of producing an emulsion as defined above and comprising ungelled plant gum, applying it to the foodstuff and gelling the gum.
- Method for preventing the transfer of moisture between constitutents of a multi-component food product comprising the step of interposing a film as defined above between the food constituents.
- Method for preventing the transfer of moisture between the atmosphere and a food product comprising the step of interposing a film as defined above between the food and the atmosphere.

2. Claims: 1 partly, 2, 3 partly, 4-6, 7 partly, 8 partly, 9, 10-26 all partly, 27, 28-75 all partly

In the field of FOODSTUFFS:

- Edible composite film for use as moisture barrier in a FOODSTUFF, the film comprising a conglomerate of lipid and hydrocolloid components, wherein the HYDROCOLLOID COMPONENTS comprises (or consists of) a STARCHY LEGUMINOUS SEED PROTEIN

or LUPIN PROTEIN.
- Dry mix for use as a hydratable base in the preparation of the above film.

- Moisture barrier system comprising as separate components, the above dry-mix and a gelling salt solution and opt. a liquid plasticiser.
- Emulsion comprising the above dry-mix in admixture with water.
- FOODSTUFF comprising the above film or emulsion.
- Process for producing an edible composite film as defined above comprising the steps of preparing a dry mix as defined above and hydrating it to produce an emulsion as defined above.
- Process for producing a foodstuff comprising the steps of producing an edible composite film by a process as defined above and applying it to the foodstuff.
- Process for producing a foodstuff comprising the steps of producing an emulsion as defined above and comprising ungelled plant gum, applying it to the foodstuff and gelling the gum.
- Method for preventing the transfer of moisture between constitutents of a multi-component food product comprising the step of interposing a film as defined above between the food constituents.
- Method for preventing the transfer of moisture between the atmosphere and a food product comprising the step of interposing a film as defined above between the food and the atmosphere.

3. Claims: 1 partly, 2 partly, 3, 4 partly, 5 partly, 6-9, 10-75 all partly

In the field of FOODSTUFFS:

- Edible composite film for use as moisture barrier in a FOODSTUFF, the film comprising a conglomerate of LIPID, a PROTEIN component, a GELLED PLANT GUM, an EMULSIFIER, WATER and opt. a buffering agent and/or a plasticiser.
- Dry mix for use as a hydratable base in the preparation of the above film.
- Moisture barrier system comprising as separate components, the above dry-mix and a gelling salt solution and opt. a liquid plasticiser.
- Emulsion comprising the above dry-mix in admixture with water.
- FOODSTUFF comprising the above film or emulsion.
- Process for producing an edible composite film as defined above comprising the steps of preparing a dry mix as defined above and hydrating it to produce an emulsion as defined above.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

- Process for producing a foodstuff comprising the steps of producing an edible composite film by a process as defined above and applying it to the foodstuff.
- Process for producing a foodstuff comprising the steps of producing an emulsion as defined above and comprising ungelled plant gum, applying it to the foodstuff and gelling the gum.
- Method for preventing the transfer of moisture between constitutents of a multi-component food product comprising the step of interposing a film as defined above between the food constituents.
- Method for preventing the transfer of moisture between the atmosphere and a food product comprising the step of interposing a film as defined above between the food and the atmosphere.

4. Claim : 55 partly

NON-FOODSTUFFS comprising the film of claims 1-41 or the emulsion of claims 52-54.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/00846

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0547551 A	23-06-93	CA 2085457 A	17-06-93
		DE 69223024 D	11-12-97
		DE 69223024 T	18-06-98
		ES 2109303 T	16-01-98
		FI 925699 A	17-06-93
EP 0465801 A	15-01-92	AU 633211 B	21-01-93
		AU 7733891 A	16-01-92
		CA 2044428 A	11-01-92
		DE 69100980 D	24-02-94
		DE 69100980 T	19-05-94
		DK 465801 T	02-05-94
		EG 19779 A	29-02-96
		ES 2049062 T	01-04-94
		FI 912950 A	11-01-92
		JP 4229146 A	18-08-92
		MX 174515 B	20-05-94
		PT 98261 A	29-05-92
		US 5401518 A	28-03-95
US 5019403 A	28-05-91	NONE	
US 5543164 A	06-08-96	NONE	
EP 0594258 A	27-04-94	NL 9201820 A	16-05-94
EP 0471558 A	19-02-92	AU 8177591 A	20-02-92
		CA 2049159 A	15-02-92
		JP 5345127 A	27-12-93
US 3323922 A	06-06-67	NONE	
FR 2590122 A	22-05-87	EP 0228319 A	08-07-87
		JP 62118846 A	30-05-87
WO 8605363 A	25-09-86	FR 2578719 A	19-09-86
		AU 584407 B	25-05-89
		AU 5548186 A	13-10-86
		CA 1272635 A	14-08-90
		DK 527086 A,B,	05-11-86

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/00846

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 8605363 A		EP 0215872 A	01-04-87
		JP 6026517 B	13-04-94
		JP 62502237 T	03-09-87
		US 4759936 A	26-07-88
EP 0643916 A	22-03-95	NONE	
US 4762721 A	09-08-88	NL 8501283 A	01-12-86
		AU 567235 B	12-11-87
		AU 5715186 A	13-11-86
		CA 1286141 A	16-07-91
		DE 3660523 A	22-09-88
		EP 0205195 A	17-12-86
EP 0486076 A	20-05-92	NL 9002273 A	18-05-92
		DE 69128767 D	26-02-98
		DE 69128767 T	10-09-98
EP 0048123 A	24-03-82	NONE	